



Preparation and properties of UV-curable multi-arms cardanol-based acrylates



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ABSTRACT

A series of multi-arms cardanol-based acrylates (CGHA, CDHA, CTHA) were synthesized using renewable cardanols and bio-based polyols (glycerol, diglycerol, tripilyglycerol) as precursors. The structures and molecular weights of the cardanol-based acrylates were characterized by FT-IR, ¹H NMR and GPC, respectively. The synthesized multi-arms cardanol-based acrylates were used to produce UV-curable films and coatings. High mechanical strength as well as good biodegradability of the UV-cured films was obtained. The important coating film properties, such as hardness, gloss and adhesion were also investigated. The results showed that the coatings with high bio-based content exhibit good adhesion, gloss and acid-resistance, which is comparable to the soybean oil (AESO)-based and polyester acrylate.

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1. Introduction

Renewable organic resources continue to be in the common interest of both academic and industrial laboratories in recent years [1]. Owing to the economy and environmental friendliness, there is growing pressure to reduce carbon dioxide emissions by fossil fuels. Therefore, developing alternate chemical feed stocks from renewable resources is essential [2]. Products of oil-bearing wild plants such as soybean, castor, gallnut, tung, linseed, veronica, etc. have made good contributions to the efforts of harnessing renewable resources [3–5]. The oils of these plants have been used in preparing a large number of useful materials such as adhesives, paints, ion-exchangers, etc. due to their specific chemical functionality. Furthermore, these materials are sometimes cheaper than petrochemicals [6].

Among the renewable resources, cardanol, which can be obtained by distillation of the cashew nut shell liquid, is one of the important renewable resources [7–9]. Cardanol generally has an unsaturated hydrocarbon chain with one to three double bonds at the meta-position of the phenol group. Cardanol based materials have been studied in various industrial applications due to the attractive characteristics such as self-cross-linkable, antibacterial, and chemically modifiable properties [10–12]. Cardanol has been used to produce phenalkamine low temperature curing agents

for the durable epoxy coatings for marine applications [13,14]. Frictional materials are made by polymerizing side chain of cardanol, followed by cross polymerization with formaldehyde to yield cardanol formaldehyde resin [15,16]. Cardanol based polyols have been developed for rigid polyurethane applications [17]. Furthermore, the physico-chemical properties of the cardanol based polymers have been improved by cross-linking reaction of the unsaturated hydrocarbon chain in the cardanol upon UV irradiation [18,19]. With its reactive functional benzene ring, phenolic hydroxyl and unsaturated alkyl chain group, cardanol can be used as a natural and renewable chemical feedstock to fine chemical products, such as solvents, coatings, varnishes, surfactants and plasticizers [19]. Despite all these uses, only a fraction of the cardanol obtained from cashew nut processing is used in the industrial field. Therefore, there is an overwhelming interest to create new materials with improved performance from cardanol for new applications.

Unsaturated esters are widely used in UV curing system because they can be cured with radical photoinitiators [20]. Vinyl ester resins (VERs), one of important unsaturated ester, are widely used in thermosetting materials and are the addition product of an epoxide resin and ethylenically unsaturated monocarboxylic acid containing ester groups and carbon-to-carbon double bond linkages at the end of the polymer chain [21,22]. Because of their network structure, they possess high tensile strength and modulus, excellent chemical and corrosion resistance as well as good dimensional stability and elevated heat distortion temperatures. Cardanol-based vinyl ester resins [23–25] have been developed

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and find innumerable applications as base materials for adhesives and thermosetting matrix materials for composites. As another important unsaturated ester, acrylates are important components for coatings that essentially determine the performances and their final applications. As well known, the UV-cured films of acrylate prepolymers possess some excellent properties, such as UV resistance and high transmittance. Khudyakov and coworkers [26] reported the synthesis of thioether and thiourethane acrylate oligomers as UV-curable high refraction oligomers. Nakayama and Hayashi [27] studied the synthesis of difunctional thiourethane methacrylate and the preparation of organic/inorganic nanocomposites. Kim et al. [28] synthesized UV-curable di-functional sulfur-containing thioacrylate and thiourethane acrylate with high refractive indices. Besides, they have the advantage of fast curing along with industrial or commercial acceptance. Thus, cardanol-based acrylates are an excellent alternative to develop new coating materials. Moreover, developing low-carbon, highly efficient and environmentally friendly technologies for coatings are necessary [29].

In this work, we reported the synthesis and properties of UV-curable multi-arms cardanol-based acrylates. The structure and molecular weight of the resin were characterized. Then, these cardanol-based multi-arms acrylates were used in UV-curing coatings. The adhesion, mechanical properties and tensile strength of the cardanol-based acrylates were discussed. The aim of the research is to synthesize a series of high bio-based content resin and explore their use in UV-curable coatings.

2. Experiment

2.1. Materials

Cardanol (Ultra LITE 2023) was kindly supplied by Cardolite Chemical Zhuhai Co., Ltd. (Guangdong, China). Isophorone diisocyanate (IPDI) was provided by Wuxi Dongrun Chemical Materials Co., Ltd. (Wuxi, China). 4-Methoxyphenol (MEHQ) was provided by Wuxi Chemical Adjuvant Agent Plant (Wuxi, China). Irgacure 184 was supplied by Ciba Specialty Chemicals Ltd. (Shanghai, China). Dibutyltin dilaurate (DBTDL) and hydrogen peroxide (50 wt% solution in water) were purchased from Aladdin (Shanghai, China). Glycerol, diglycerol, triglycerol were purchased from Jinan Dowin Chemical Technology Co., Ltd. (Jinan, China). Triphenylphosphine (TPP), sodium bicarbonate, acrylic acid, ethyl acetate and n-butylacetate were purchased from Sinopharm Chemical Reagent Co., Ltd. (Shanghai, China). Diphenyl (2,4,6-trimethylbenzoyl)phosphine oxide (TPO) was purchased from Guangzhen Photosensitive materials Co., Ltd. (Foshan, China). Acrylated epoxidized soybean oil (AESO) was provided by Jiangsu SanMu Group Co., Ltd. (Wuxi, China). Polyester acrylate (CN2302) was purchased from Sartomer (USA) Chemicals Co., Ltd. All materials were used as received without further purification.

2.2. Synthesis of cardanol-based multi-armed acrylates

2.2.1. Synthesis of NCO-terminated unsaturated monomer (CI)

The reactions were carried out in a 125 ml three-neck flask in oil bath which was equipped with a thermometer, a mechanical stirrer, a dropping funnel and a cold water condenser. IPDI (22.29 g) was charged to the reaction flask. The temperature was raised to 55 °C while Ultra LITE 2023 (29.99 g) and DBTDL (0.021 g, 0.04 wt% of reactions) mixture was dropped into the flask for 2 h. Afterwards, the reactions were stirred at 45 °C. Until the theoretical value of –NCO groups were reached. NCO-terminated unsaturated monomer (CI) was obtained (Fig. 1).

2.2.2. Synthesis of cardanol-based full-capped isocyanate (CIG)

Glycerol (3.07 g) were charged into a 125 ml three-neck flask in oil bath equipped with a thermometer, a mechanical stirrer, a dropping funnel and a condenser, and the temperature was raised to 70 °C. CI (52.20 g) dissolved with methylbenzene while added DBTDL (0.022 g, 0.04 wt% of reactions), and the mixture was dropped into the flask for 1 h. When the reaction reached an NCO value of 0.5 or less to 0.5, the cardanol-based full-capped isocyanate (CIG) was obtained.

2.2.3. Synthesis of cardanol-based epoxy oligomers (CGH)

CIG (55.20 g), methylbenzene (50.0 g) and formic acid (5.23 g) were charged into a 125 ml three-neck flask in oil bath equipped with a thermometer, a mechanical stirrer. Hydrogen peroxide (50 wt% aqueous solution, 27.20 g) was dropped into the flask. After the completion of the hydrogen peroxide addition, the reaction was stirred at 50 °C for 10 h. Afterwards, the solution washed three times with sodium bicarbonate (50 wt% aqueous solution) followed by washing three times with water. Cardanol-based epoxy oligomers (CGH) were obtained by evaporating the methylbenzene.

2.2.4. Synthesis of cardanol-based three-armed acrylate (CGHA)

CGH (45.29 g), TPP (0.84 g, 1.5 wt%) as catalyst, MEHQ (0.08 g, 0.1 wt%) as inhibitor were charged into a 125 ml three-neck flask in oil bath equipped with a thermometer, a mechanical stirrer and the temperature was raised to 95–100 °C. Acrylic acid (11.10 g) was dropped into the flask for 0.5–1 h. When the acid value reached to 5 or less to 5, the cardanol-based three-armed acrylate (CGHA) was obtained.

The same procedure was followed for the synthesis of cardanol-based four-armed acrylate and cardanol-based five-armed acrylate, except diglycerol, polyglycerol was used in second stage instead of glycerol, respectively.

2.3. Characterization

Real-time Fourier transform infrared (RTIR) measurements were performed by using a Nicolet 6700 FTIR spectrometer from Thermo Scientific with an extended range KBr beam-splitter and an MCT/A detector. An EfosLite mercury vapor curing lamp equipped with a fiber optic light guide was the source for UV irradiation of samples. Uncured sample was exposed to UV light for 10 min at intensity of 30.0 mW/cm². The radiation intensity was measured using a UV light meter (UV-integrator140, 250–410 nm, Kühnast Radiation Technology Limited Liability Company, Germany). All the samples were cured at room temperature and performed without air. The reaction progression was followed by monitoring the change in absorption of the acrylate peak at 810 cm⁻¹. In order to calculate conversion from the absorption data, equation was used:

$$\text{Degree of conversion} = \left[\frac{[(A)_{810}]_0 - [(A)_{810}]_t}{[(A)_{810}]_0} \right] \times 100$$

König hardness (PH-5858, BYK, Germany) was the testing mode (ASTM D 4366), with the values reported in seconds (s). Pencil hardness (BY, Shanghai Pushen Chemical Machinery Co., Ltd.) was measured using ASTM D 3363. Adhesion test (QFH, Tianjin Jingke material testing machine factory) was performed using the standard crosshatch adhesion test (ASTM D 3359). The Fourier transfer infrared (FT-IR) spectra (ABB BOMEN, Canada) were collected using an ABB BOMEN FTLA 2000-104 spectrometer with a KBr disk. The proton nuclear magnetic resonance (¹H NMR) spectra were collected with a Bruker Avance Digital 400 MHz (Bruker, Switzerland) spectrometer using tetramethylsilane as an internal reference and dimethylsulfoxide (DMSO) as a solvent. The

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